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SYNTHESIS AND CRYSTAL STRUCTURE OF CADMIUM(II) DICHLOROASAALICYLIDENESEMICARBAZONE

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Abstract: Cadmium(II) complex with salicyl aldehyde semicarbozone (H₂L) has been synthesized. Based on elemental analysis and IR spectroscopy its composition – [Cd·H₂L·H₂O·Cl₂] – has been established. The complex crystal structure has been examined using XRD analysis. The coordination polyhedron of cadmium atom is a distorted octahedron, where two *cis*-positions are occupied by oxygen atoms of water molecule and carbamide fragment of H₂L molecule, other positions are occupied by chlorine atoms. At the same time two edges of octahedron are combined with adjoined octahedrons and form endless zigzag chains of octahedrons in the structure along the crystallographic axis. H₂L molecule is

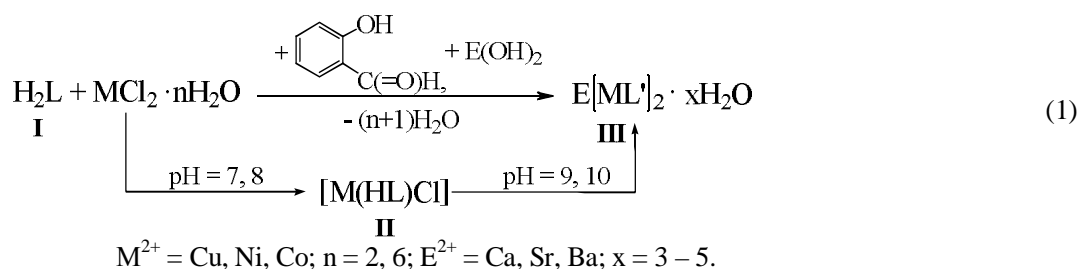
a planar one due to the presence of intramolecular hydrogen bond.

Keywords: cadmium, salicylidene semicarbazone, XRD.

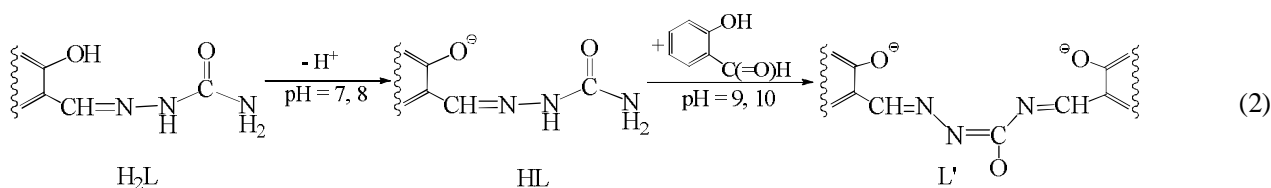
1. Introduction

In modern coordination chemistry Schiff base plays a role of universal ligands. The complexes on its basis have valuable practical properties: antibacterial [1-3], catalytic [4] and may be used as precursors [5]. Salicyl aldehyde semicarbazone (H₂L) forms various complexes with cations of transition metals and behaves as mono- or bidentate ligand [6-8].

Previously [9] we synthesized new heterometal complexes of cuprum(II), nickel(II) and cobalt(II) with N,N'-bis(salicylidene)semicarbazide(L') **III** according to Eq. (1):



It was shown that complexation is accompanied by sequential changes of ligand part in the following consequence (H₂L → HL → L'):



At the same time we considered the complexes **II** as synthesis intermediates of the final complexes **III**.

To extend the nomenclature of the synthesized complexes **III** and study their physico-chemical properties we introduced cadmium(II) compounds into Eq. (1). However, while using cadmium chloride we obtained light-yellow crystals which do not correspond to intermediate **II** or final complex **III** according to the results of elemental analysis. Thus, different by structure and composition complexes may be obtained depending on metal nature. The reason is complexing activity of used transition metals which in the first approximation correspond to empirical row of Irving-Williams: $\text{Ca}^{2+} < \text{Mg}^{2+} < \text{Mn}^{2+} < \text{Fe}^{2+} < \text{Cd}^{2+} < \text{Co}^{2+} < \text{Zn}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+}$. Taking into account all above-mentioned, the work deals with the results of elemental analysis, IR spectroscopy and XRD study of cadmium with salicyl aldehyde semicarbazone complex $[\text{Cd}\cdot\text{H}_2\text{L}\cdot\text{H}_2\text{O}\cdot\text{Cl}_2]$ (**IV**).

2. Experimental

To synthesize salicylic aldehyde semicarbazone (H_2L) and complex **IV** we used muriatic semicarbazide, salicylic aldehyde, CH_3COONa , CdCl_2 and $\text{Ba}(\text{OH})_2$ of high purity.

FT-IR analysis was performed using Nicolet iS10 spectrometer within the range of $4000\text{--}375\text{ cm}^{-1}$. The samples were examined as received, without pretreatment.

The contents of cadmium in the compound **IV** was determined on the basis of complexometric titration [10] after complex previous thermal decomposition in a mixture of concentrated nitric and sulfuric acids. The nitrogen content in the H_2L and compound **IV** was determined by Dumas method [11].

2.1. Synthesis of H_2L

H_2L was prepared by mixing 1.12 g (0.01 mol) of muriatic semicarbazide, 1.22 g (0.01 mol) of salicylic aldehyde and 0.82 g (0.01 mol) CH_3COONa in 50 ml of water-ethanol mixture (1:1). The reaction mass was stirred under heating at 333 K for 30 min. After mixture cooling the light-yellow deposit was filtered using Schott filter, washed with cold ethanol and dried in an air at room temperature till the mass became constant. The yield was 1.71 g (95.5 %). Found, %: N 23.18. For $\text{C}_8\text{H}_9\text{N}_3\text{O}_2$. Calc., %: N 23.46.

2.2. Synthesis of $[\text{Cd}(\text{C}_8\text{H}_9\text{N}_3\text{O}_2)(\text{H}_2\text{O})\text{Cl}_2]_n$ (**IV**)

1.79 g (0.01 mol) of salicyl aldehyde semicarbazone were dissolved in 50 ml of ethanol at 333 K using water bath. Aqueous-alcohol solution of

$\text{Ba}(\text{OH})_2$ was added to the hot solution by portions till pH became 9–10. Then 1.22 g (0.01 mol) of salicylic aldehyde was added. Next 1.83 g (0.01 mol) of cadmium chloride dissolved in 40 ml of ethanol were introduced into the reaction mass at 333 K under constant stirring. The reaction mass was sustained for 1 h, then cooled and additionally filtered using Schott filter.

The filtrate of light-yellow color was left for a month. During slow evaporation light-yellow crystals of cadmium(II) dichloroaquasalicylidenesemicarbazone suitable for XRD were precipitated. The yield was 2.77 g (85 %). Found, %: N 10.86, Cd 29.71. For $\text{C}_8\text{H}_{11}\text{N}_3\text{O}_3\text{Cl}_2\text{Cd}$. Calc., %: N 11.04, Cd 29.54.

2.3. X-ray Crystallography

X-ray diffraction study of $[\text{Cd}(\text{C}_8\text{H}_9\text{N}_3\text{O}_2)(\text{H}_2\text{O})\text{Cl}_2]_n$ **IV** was carried out using Xcalibur-3 automated diffractometer (Oxford Diffraction Ltd), ($\text{MoK}\alpha$ -radiation, graphite monochromator, Sapphire-3 CCD-detector). Structure was solved by direct methods and refined by the least squares using SHELX-97 program package [12]. Hydrogen atoms were located on the difference map and refined using the riding model excluding those belonging to the amino group and water molecule which were refined isotropically with common B_{iso} . The WinGX [13] and Balls&Sticks [14] programs were used for the analysis of structure and figures preparation.

3. Results and Discussion

The comparative analysis of IR-spectra for H_2L ligand and complex **IV** shows the invariability in the deformational vibrations of aromatic cycle OH-groups band within $1270\text{--}1215\text{ cm}^{-1}$ and main absorption bands $n_{\text{as}}(\text{NH}_2)$ 3410 cm^{-1} , $n(\text{NH})$ 2987 cm^{-1} , $n(\text{C}=\text{N})$ 1590 cm^{-1} . At the same time, the absorption band in the IR-spectrum of the complex **IV** $n(\text{C}=\text{O})$ shifts by 40 cm^{-1} toward high area compared with that of H_2L . Thus, we assume that only the carbonyl group oxygen reacts with a metal and the phenol hydroxide oxygen does not participate in the coordination with the cadmium atom.

Crystal structure **IV** consists of cadmium cation coordinated by two chlorine ions, as well as by molecules of salicyl aldehyde semicarbazone molecules (H_2L) and water – $[\text{Cd}\cdot\text{H}_2\text{L}\cdot\text{H}_2\text{O}\cdot\text{Cl}_2]$. Coordination number of cadmium in polyhedron of distorted octahedron is equal to 6. The scheme of atoms numeration and ellipsoids of heat vibrations in the independence part of the cell are represented in Fig. 1.

The main crystallographic data and revised results concerning $[\text{Cd}\cdot\text{H}_2\text{L}\cdot\text{H}_2\text{O}\cdot\text{Cl}_2]$ complex are represented in Table 1.

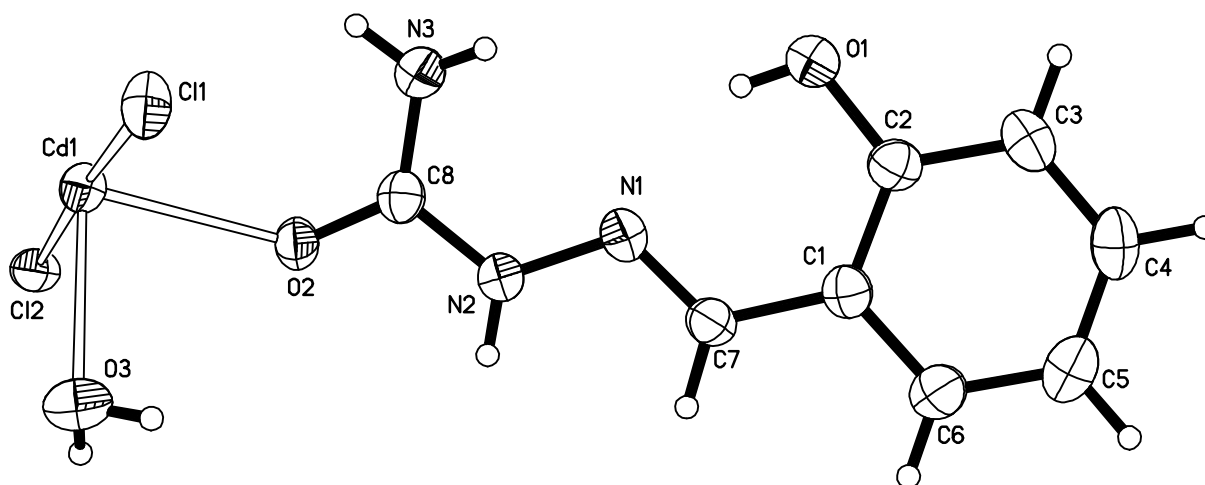


Fig. 1. Atomic numbering scheme and thermal ellipsoids (50 % probability level) for $[\text{Cd}\cdot\text{H}_2\text{L}\cdot\text{H}_2\text{O}\cdot\text{Cl}_2]$, IV

Table 1

Crystal data and structure refinement results for $[\text{Cd}\cdot\text{H}_2\text{L}\cdot\text{H}_2\text{O}\cdot\text{Cl}_2]$, (IV)

Empirical formula	$\text{C}_8\text{H}_{11}\text{CdCl}_2\text{N}_3\text{O}_3$
Formula weight M_r , a.m.u.	380.50
Temperature, K	293(2)
Wavelength $\text{MoK}\alpha$, Å	0.71073
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions, Å, °	$a = 6.6359(3)$, $\alpha = 77.641(3)$, $b = 6.9465(2)$, $\beta = 76.833(3)$, $c = 14.0811(5)$, $\gamma = 78.015(3)$
Cell volume V , Å ³	608.70(4)
Z , d_{calc}	2, 2.076 g/cm ³
Absorption coefficient $\mu(\text{MoK}\alpha)$, mm ⁻¹	2.231
F_{000}	372
Crystal size, mm	0.40×0.09×0.05
q range for data collection, °	$3.04 \leq \theta \leq 26.00$
Index ranges	$-6 \leq h \leq 8$, $-7 \leq k \leq 8$, $-17 \leq l \leq 17$
Reflections collected/unique	5677/2379 ($R_{\text{int}} = 0.0252$)
Completeness to $2\theta = 26.00^\circ$	99.0 %
Transmission $T_{\text{max}}/T_{\text{min}}$	0.8966/0.4689
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2379/4/170
Goodness-of-fit on F^2	0.992
Final R indices ($I > 2\sigma(I)$)	$R_F = 0.0218$, $wR^2 = 0.0458$
R indices (all data)	$R_F = 0.0255$, $wR^2 = 0.0477$
Largest diff. hole and peak $\Delta r_{\text{min}}/\Delta r_{\text{max}}$, e·Å ⁻³	-0.302/0.624

Table 2

Selected bond distances and angles (Å, °) in the coordination polyhedron for the structure IV

Bond	<i>d</i> , Å	Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
Cd(1)-O(3)	2.3406(12)	Cl(2)-Cd(1)#2	2.6715(4)	C(1)-C(6)	1.400(2)
Cd(1)-O(2)	2.3427(11)	O(1)-C(2)	1.367(2)	C(1)-C(2)	1.401(2)
Cd(1)-Cl(1)#1	2.5674(4)	O(2)-C(8)	1.250(2)	C(1)-C(7)	1.445(2)
Cd(1)-Cl(1)	2.5764(5)	N(1)-C(7)	1.284(2)	C(2)-C(3)	1.388(3)
Cd(1)-Cl(2)	2.6069(5)	N(1)-N(2)	1.370(2)	C(3)-C(4)	1.380(3)
Cd(1)-Cl(2)#2	2.6715(4)	N(2)-C(8)	1.348(2)	C(4)-C(5)	1.374(3)
Cl(1)-Cd(1)#1	2.5673(4)	N(3)-C(8)	1.324(2)	C(5)-C(6)	1.375(3)
Angle	<i>w</i> , °	Angle	<i>w</i> , °		
O(3)-Cd(1)-O(2)	81.85(4)	H(3C)-O(3)-H(3D)	102.4(6)		
O(3)-Cd(1)-Cl(1)#1	95.14(3)	C(7)-N(1)-N(2)	116.00(13)		
O(2)-Cd(1)-Cl(1)#1	176.81(3)	C(8)-N(2)-N(1)	122.13(13)		
O(3)-Cd(1)-Cl(1)	86.84(4)	C(8)-N(3)-H(3A)	117.0(13)		
O(2)-Cd(1)-Cl(1)	91.35(3)	C(8)-N(3)-H(3B)	116.6(9)		
Cl(1)#1-Cd(1)-Cl(1)	89.544(15)	H(3A)-N(3)-H(3B)	122.1(17)		
O(3)-Cd(1)-Cl(2)	90.68(3)	C(6)-C(1)-C(2)	117.57(16)		
O(2)-Cd(1)-Cl(2)	86.35(3)	C(6)-C(1)-C(7)	119.19(15)		
Cl(1)#1-Cd(1)-Cl(2)	92.636(14)	C(2)-C(1)-C(7)	123.24(16)		
Cl(1)-Cd(1)-Cl(2)	176.840(13)	O(1)-C(2)-C(3)	118.00(15)		
O(3)-Cd(1)-Cl(2)#2	168.75(3)	O(1)-C(2)-C(1)	121.29(15)		
O(2)-Cd(1)-Cl(2)#2	86.90(3)	C(3)-C(2)-C(1)	120.71(16)		
Cl(1)#1-Cd(1)-Cl(2)#2	96.102(14)	C(4)-C(3)-C(2)	119.60(17)		
Cl(1)-Cd(1)-Cl(2)#2	93.681(14)	C(5)-C(4)-C(3)	121.00(17)		
Cl(2)-Cd(1)-Cl(2)#2	88.364(13)	C(4)-C(5)-C(6)	119.33(17)		
Cd(1)#1-Cl(1)-Cd(1)	90.455(15)	C(5)-C(6)-C(1)	121.76(17)		
Cd(1)-Cl(2)-Cd(1)#2	91.637(13)	N(1)-C(7)-C(1)	122.31(15)		
C(8)-O(2)-Cd(1)	130.06(10)	O(2)-C(8)-N(3)	123.49(15)		
Cd(1)-O(3)-H(3C)	110.0(7)	O(2)-C(8)-N(2)	117.53(14)		
Cd(1)-O(3)-H(3D)	106.0(6)	N(3)-C(8)-N(2)	118.96(15)		

Symmetry operations for the obtaining equivalent atoms:

#1: -x+3,-y,-z; #2: -x+2,-y,-z

Table 3

Characteristics of hydrogen bonds D-H...A in the complex IV

Contact D-H...A	Distance, Å			Angle DHA, °
	d(D-H)	d(H...A)	d(D..A)	
O(1)-H(1)...N(1)	0.79	1.97	2.6630(18)	145.9
O(3)-H(3C)...O(2)#3	0.821(4)	1.977(5)	2.7927(17)	172.8(10)
O(3)-H(3D)...Cl(2)#3	0.819(4)	2.705(7)	3.3551(13)	137.6(7)
N(2)-H(2)...Cl(2)#3	0.83	2.61	3.3504(14)	149.9
N(3)-H(3A)...O(1)#4	0.835(8)	2.476(13)	3.122(2)	134.9(15)
N(3)-H(3B)...Cl(2)#2	0.835(9)	2.606(11)	3.3859(15)	155.9(14)

Symmetry operations for the obtaining equivalent atoms:

#1: -x+3,-y,-z; #2: -x+2,-y,-z; #3: -x+2,-y+1,-z; #4: -x+2,-y,-z+1

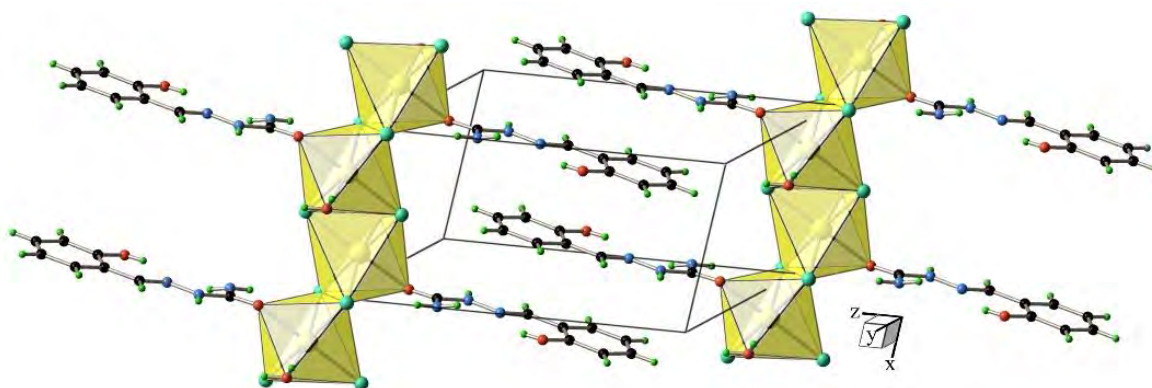


Fig. 2. Layer structure in the complex IV

Table 2 represents the values of bond length and valence angles formed by non-hydrogenous atoms in the structure. Hydrogen bonds are shown in Table. 3. The atomic coordinates are deposited in the Cambridge database (CCDC 1035625) and may be obtained from <https://www.ccdc.cam.ac.uk/deposit> on request.

According to XRD data (Fig. 1) the independence part of the cell contains cadmium atom, two chlorine atoms, molecule of neutral ligand $C_8H_9N_3O_2$ (H_2L), and water molecule. At the same time cadmium atom in polyhedron of distorted octahedron is coordinated by two oxygen atoms of water and ligand carbamide fragment being in *cis*-positions. The rest four positions are occupied by chlorine atoms (coordination unit CdO_4Cl_2). They compose two edges of adjoined octahedrons and form endless zigzag chains of octahedrons along the crystallographic axis X (Fig. 2). In the mentioned coordination unit (Fig. 1, Table 2) interatomic distances $Cd(1)-O(2)$, $Cd(1)-O(3)$, $Cd(1)-Cl(1)$ и $Cd(1)-Cl(2)$ are equal to 2.3427(11), 2.3406(12), 2.5764(5) and 2.6069(5) Å, respectively. The values of bond $Cd(1)-O(2)$ relate to the coordination of the central atom and oxygen of carbamide group; $Cd(1)-O(3)$ bond – to the coordination bond with oxygen of water molecule. In the complexes with similar ligands – salicyl aldehyde semicarbazone (chelate unit CuO_2NCl [15]) the length of copper-oxygen bond in phenyl fragment is 1.918(6) Å, and in carbamide fragment – 1.997(6) Å. The comparison of bond lengths of chelate unit CuO_2NCl and complex IV (coordination unit CdO_4Cl_2) exhibits that in our case the deprotonation of salicyl aldehyde semicarbazone does not take place and coordination proceeds via oxygen atom of carbamide only. This result is in agreement with general concept about chemical bonding and its energy in the coordination compounds of chelate type. The comparison of bond lengths of the investigated complex CdO_4Cl_2 and cadmium complex with salicyl aldehyde condensation product and 3-(pyridine-2-yl)-5-(2-aminophenyl)-1H-

1,2,4-triazol (chelate unit of binuclear complex CdO_4N_2) [16] confirms the above-mentioned fact. The length of bond $Cd(1)-O(3)$ in CdO_4Cl_2 and CdO_4N_2 complexes is equal to 2.3406(12) and 2.3282 Å, respectively, which confirms coordination of cadmium atom relative to oxygen atom of carbonyl ($>C=O$) group. Other values of bond length and valence angle for molecular ligands of the complex IV have usual magnitudes and do not require comments [17].

H_2L molecule is a planar one with accuracy of 0.05 Å due to the presence of intramolecular hydrogen bond $O(1)-H(1)...N(1)$ (Table 3). Maximum deviations from mean square plane are observed for the end atoms of urea fragment $O(2)$ (-0.128 Å) and $N(3)$ (0.061 Å). Planar molecules H_2L , which belong to diagonally arranged octahedron chains [011], are staked in a pile and form close packed layers together with the chains in a plane $(0\bar{1}1)$ (Fig. 2). Hydrogen bonds are observed between adjoined layers. Bond characteristics are represented in Table 3.

To conclude it should be noted that there are some short contacts $N...H$ of carbamide group nitrogen atom and hydrogen atom of coordinated water molecule responsible for the possible formation of intramolecular H-bonds. The characteristics of such hydrogen bonds are represented in Table 3.

4. Conclusions

The new cadmium(II) complex with salicyl aldehyde semicarbazone (H_2L) has been synthesized. Its composition – $[Cd H_2L H_2O Cl_2]$ was established using chemical analysis and IR spectroscopy. The cadmium(II) complex crystal structure was examined using XRD analysis. The coordination polyhedron of cadmium atom is a distorted octahedron, where two *cis*-positions are occupied by oxygen atoms of water molecule and

carbamide fragment of H_2L molecule, other positions are occupied by chlorine atoms. Coordination number of cadmium in polyhedron of distorted octahedron is equal to 6.

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СИНТЕЗ І КРИСТАЛІЧНА СТРУКТУРА ДИХЛОРОАКВАСАЛІЦИЛІДЕНСЕМІКАРБАЗОН У КАДМІЮ(II)

Анотація. Синтезовано комплекс кадмію(II) із семикарбазоном саліцилового альдегіду (H_2L). За допомогою елементного аналізу та ІЧ-спектроскопії встановлено його склад – $[CdH_2LH_2O \cdot Cl_2]$. Кристалічну структуру комплексу досліджено за допомогою методу РСА. Встановлено, що координаційним поліедром атому кадмію є деформований октаедр, в якому два цис-положення займають атоми кисню молекули води і карбамідного фрагменту молекули H_2L , решту положень займають атоми хлору. Показано, що два ребра октаедра є спільними із сусідніми октаедрами, за рахунок чого в структурі утворюються безкінечні зигзагоподібні ланцюги октаедрів уздовж кристалографічної осі. Молекула H_2L є плоскою завдяки наявності внутрішньо-молекулярного водневого зв'язку.

Ключові слова: кадмій, саліциліденсемікарбазон, рентгеноструктурний аналіз.